A Study of Triarylmethyls Containing Sulfur

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By
Wesley Minnis

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AN ACKNOWLEDGMENT

This investigation was made with the assistance of The National Aniline and Chemical Company Fellowship. I wish to express my obligation for the aid thus received.

For the inspiration received from Professor M. Gomberg and for his helpful guidance in the course of the work, I offer my sincere thanks.

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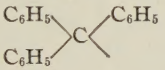
A STUDY OF TRIARYLMETHYL CONTAINING SULFUR

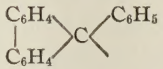
Introduction

The substance, triphenylmethyl (I), was the first definitely isolable example of the long-sought-for radicals which could exist "free," *i. e.*, with a single unsaturated carbon valence. Quite naturally, other examples of trivalent carbon were desired in order to increase our knowledge of these "free radicals," so that generalizations might be made on a broader fact foundation than the study of only one such substance provided. More or less complete studies of a large number of similar "triarylmethyls" are now to be found in the chemical literature.

The first variation from the parent substance was the preparation of radicals with substituents in the phenyl nucleus—homologs, such as diphenyl-*p*-tolylmethyl, tri-*p*-tolylmethyl, the nitrated and the halogenated triphenylmethyls. A second extension was the preparation of analogs. The phenyl nucleus was replaced by another carbocyclic ring, the naphthyl group. Elimination of two hydrogen atoms from two phenyl groups gave a biphenylenephenylmethyl (II). A further step was to radicals contain-

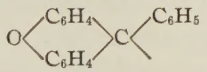


I

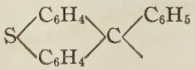


II

ing atoms of elements other than carbon and hydrogen, with heterocyclic nuclei. The first such radicals were those in which two phenyl groups were joined, not by a common valence as in the biphenylene, but by a bridge atom, such as oxygen (III), sulfur (IV), or nitrogen (V). These deriva-

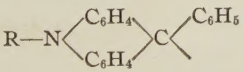


III

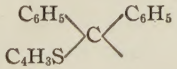


IV

tives of xanthone, thioxanthone and acridine showed essentially the same behavior as the triphenylmethyls. Few instances can be found of attempts to replace entirely a benzene ring by a distinct heterocyclic group, such as the thiophene nucleus. The latter would give the free radical, diphenylthienylmethyl (VI).



V



VI

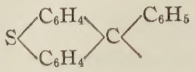
The work now reported is an extension of our knowledge of free radicals with heterocyclic structures. An example of each type has been studied; namely, phenylthioxanthyl (IV), with a sulfur bridge atom, and diphenylthienylmethyl (VI), with a distinct sulfur-containing nucleus.

A secondary aim for this research developed during the synthetic work preceding preparation of the second radical. Outside of the more simple

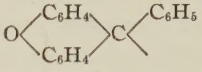
compounds, and in certain specialized fields, little investigation has been made of the chemistry of thiophene and its derivatives. In view of the numerous analogies and comparisons drawn between phenyl and thienyl compounds, it seemed desirable to test the relationship of the more complex derivatives. To this end considerable time was devoted to synthetic study of thiophene analogs of the di-, tri- and tetra-phenylmethane compounds.

Part I. Phenylthioxanthyl

The free radical, phenylthioxanthyl (I), differs structurally from phenylxanthyl (II) only in the substitution of a sulfur for an oxygen atom.



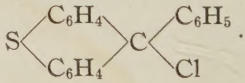
I



II

The difference in the degree of dissociation of the dimolecular forms of these two radicals, as reported in the literature, is therefore quite perplexing. Schlenk and Renning[1] found 82% of the latter substance to be monomolecular by determining the molecular weight in a boiling benzene solution of 1.5% concentration, while they report only 14% of the former to be monomolecular in freezing benzene (0.7% solution). A later investigation[2] showed phenylxanthyl to be 70% monomolecular in freezing naphthalene (1.5% solution).

As Schmidlin[3] justly observes, molecular-weight determinations of free radicals are of value only when accompanied by the determinations of oxygen absorption. Otherwise unnoticed transformations or isomerizations of the radicals may vitiate the results. The results of Gomberg and Schoepfle on phenylxanthyl were checked by parallel oxygen absorptions; it now seemed desirable to repeat the investigation of phenylthioxanthyl, controlling the work by this essential test.

Phenylthioxanthenol Chloride, 

. —Phenylthioxanthenol was prepared from thioxanthone and phenyl magnesium bromide,[4] the thioxanthone having been made from thiosalicylic acid.[5] The xanthenol used in this work was recrystallized from hot petroleum ether (100–110°), and had a melting point of 105° or over.

The red additive compound, phenyl-quino-thioxanthenol chloride-hydrochloride[6] was made by passing a slow stream of dry hydrogen chloride into a concentrated ethereal solution of the carbinol. It is quite insoluble in this solvent. The red crystals were quickly filtered, washed and dried in a vacuum desiccator over sulfuric acid.

Various procedures were investigated in order to arrive at the most satisfactory method for removing the extra molecule of hydrochloric acid. The simplest procedure

proved to be the best. Ten g. of chloride-hydrochloride was suspended in 100 cc. of dry benzene in a distilling flask which carried an extra side arm sealed into the bulb. Through a glass tube inserted in this side arm there bubbled through the liquid a stream of air, dried by passing through conc. sulfuric acid and phosphorus pentoxide. The flask was heated in a glycerine bath to 90°, the solid gradually went into solution and the deep red color lightened considerably. The solvent was completely distilled in the course of $1^1/_2$ hours, the last portion being removed under reduced pressure to avoid superheating. On cooling, the deep red oil became a mass of lighter colored crystals, from which after recrystallization from a large quantity of dry ether in the absence of moist air, colorless crystals of chloride were obtained. They turned reddish when dried in a stream of air, in spite of most efficient drying systems. Once dry, the crystals could be preserved in a vacuum desiccator for a long time with little change. Yield 60 to 70%.

Anal. Calcd. for $C_{19}H_{13}ClS$: Cl, 11.50. Found: 11.30.

In this preparation, heating for too long a period gives a deep red gum which will not crystallize, or else crystallizes as an impure product, and in lower yield.

Oxygen Absorptions.—The preparation of the free radical is difficult because of the sensitivity of the chloride to traces of water, with which it forms carbinol and hydrochloric acid, retaining the latter as the additive salt. The presence of free acid has been shown repeatedly to be harmful to the existence of a free radical. The instability of this free radical, as indicated by the following data, may be due to the influence of acid, although it is also possible that the radical spontaneously polymerizes because of other influences, *e. g.*, light, heat. The nature of the solvent is clearly an important factor, so far as the speed of the change is concerned.

Wt. of chloride G.	Time of shaking Hours	Oxygen Absorbed Cc. (N. T. P.)	Per cent of Calc.
	Using Bromobenzene as Solvent		
0.5630	0.5	21.3	104.4
.4536	0.5	18.0	109.1
.7535	1.0	27.2	99.3
.6840	5.25	25.3	102.0
.6080	18.0	19.5	88.2
.5953	41.0	14.6	67.6
.3971	[a]	14.0	97.2
	Using Benzene as Solvent		
0.8600	0.5	29.8	95.5
.5800	0.5	20.2	95.7
.5399	0.5	15.5	79.1
.5480	0.5	15.5	77.9
.5725	0.5	17.1	82.2
.8425	0.5	25.9	84.6
.7976	1.0	23.5	81.0
.8940	3.0	24.7	76.0
.8200	3.0	18.5	62.1
.4848	6.0	7.5	42.6
.4777	14.5	4.6	26.6

[a] Shaken with solvent and silver in absorption apparatus.

All measurements were made by sealing chloride, molecular silver and the solvent in a glass tube, shaking at room temperature for the specified time, and measuring the absorption of oxygen in the usual apparatus.[7]

This record of the progressive disappearance of the free radical in solution, as time elapses, makes its instability most apparent and indicates the improbability of isolating it in the solid state.

Attempts to Isolate the Free Radical.—Preliminary trials with chloride and silver, shaken in ether, acetone or ethyl acetate, showed the latter two to be undesirable, since the brown-red solutions changed to a straw-yellow in 24 hours. The free radical in solution possesses high tinctorial power; no difference in shade or depth of color can be noted between benzene or bromobenzene solutions giving either high or low values for oxygen absorption, so that the qualitative test of decolorization with oxygen is misleading unless accompanied by the quantitative measure of absorption.

Using ether as solvent, chloride and silver were shaken one hour. On working up in the usual manner, a dark oil was obtained which changed to light red crystals in the course of a day. These crystals could not be redissolved in a large quantity of ether, showing that the original soluble product was no longer present. Redissolved in benzene and treated with petroleum ether, they formed a light pink precipitate without crystalline structure. This material did not absorb oxygen, did not contain chlorine and did not melt under 240°.

Since bromobenzene solutions appeared to be relatively stable, these were used with a 30-minute shaking period. To avoid the high temperature otherwise necessary to distil the solvent, distillation was dispensed with altogether. A large amount of petroleum ether was added to the solution precipitating a red-brown amorphous mass, which, when washed with ether, became light pink. The test for oxygen absorption was made on the final dry product within 5 hours from the beginning of the experiment, but no oxygen was absorbed.

The procedure of Schlenk and Renning[1] was next duplicated. Copper bronze ("Naturkupfer C," which they also had used) was washed with alcohol and with ether, and dried in a stream of hydrogen at 250° for 3 hours. Its efficiency was demonstrated by preparing triphenylmethyl in boiling benzene solution under exactly the same conditions used later for phenylthioxanthyl. Four and four-tenths grams of pure phenylthioxanthenol chloride and 20 g. of copper bronze were placed in a flask and protected by an atmosphere of carbon dioxide. Sixty cc. of dry thiophene-free benzene was admitted and heated to the boiling temperature in a glycerine bath. A stream of dry carbon dioxide was passed through the apparatus during the whole time of heating. Ten minutes was required to bring the benzene to boiling, heating was continued for 45 minutes and the red-brown

solution was filtered into the free radical apparatus, together with 15 cc. of warm benzene. The solvent was evaporated under reduced pressure to $^1/_3$ its volume and cooled. Since no precipitate appeared, petroleum ether was added and cooling continued overnight. Only a slight deposit of dark red-brown crystals had formed by the next morning, so a large quantity of petroleum ether was used, which threw down a pink amorphous solid. The mother liquor was removed and the product dried at room temperature in a stream of carbon dioxide. Yield, 3.0 g.

Oxygen absorption: 0.5763 g. of substance in xylene solution absorbed 1.3 cc. (N. T. P.) of oxygen, which is 5.5% of the calculated absorption for pure free radical.

The experiment was repeated with the precipitation of the product with petroleum ether immediately after partial evaporation of the solvent, so that the oxygen absorption was measured 4 hours from the beginning of the operation. The product did not absorb oxygen.

The material obtained in this manner is soluble in benzene, xylene, chloroform and carbon disulfide, giving rich wine-red solutions; it is slightly soluble in warm acetone and is insoluble in ether, petroleum ether and gasoline. Several reprecipitations from benzene solution by petroleum ether gave a colorless amorphous solid, which decomposed at 300° to 302°. It is apparently identical with the products obtained under the other procedures. In no case could any peroxide be isolated.

As a final check upon the possibility of making the free radical by this last method, oxygen absorptions were taken on benzene solutions of chloride which had been boiled with copper bronze. At the end of the heating period the tubes containing the solutions were filled with benzene, cooled to room temperature and sealed. During the entire operation the solutions were under an atmosphere of dry hydrogen. The following measurements were made.

1.0169 g. of chloride, boiled for one hour, absorbed 25.2 cc. (N. T. P.) of oxygen, or 68.3% of the calculated quantity.

0.6516 g. of chloride, boiled for one hour, then allowed to stand for two hours at room temperature, absorbed 15.7 cc. (N. T. P.) of oxygen, or 66.5%.

0.7475 g. of chloride, boiled for three hours, absorbed 12.8 cc. (N. T. P.) oxygen, or 47.2%.

From these experiments it is concluded that the material obtained by Schlenk and Renning was not the free radical, phenylthioxanthyl, and that their values for the molecular weight and degree of dissociation of this radical should be rejected.

Part II. Diphenylthienylmethyl and Other Thiophene Compounds

Only two previous attempts to obtain a free radical containing a thiophene nucleus are on record. A preliminary attempt was made by Gom-

berg and Jickling[8] to isolate the free radical, diphenylthienylmethyl; and they reported difficulty in the study because of the instability of the radical. Several years later Schlenk and Ochs[9] attempted to make trithienyl carbinol, doubtless intending to make the free radical from its chloride. They were not able to crystallize the carbinol except as its salt with perchloric acid, and have gone no further with the work.

The work of Gomberg and Jickling on diphenylthienyl carbinol and its methyl has now been continued in detail. Their findings on the instability of this free radical have been completely confirmed; and similarly to the results with phenylthioxanthyl, no isolation of the solid free radical could be made. Although the evidence is meager since based upon these two instances only, yet it is tentatively suggested that the presence of a bivalent, ring-sulfur atom in its structure confers instability upon a free radical. An increase in the valence of the sulfur atom in the only case on record, 2,2′-sulfonidotriphenylmethyl,[10] led to a free radical of greater stability.

In conjunction with the study of diphenylthienylmethyl, studies were made of related thiophene compounds. In general, methods of synthesis used in the benzene series were successfully applied. Usually the thiophene analogs were isolated with more difficulty, probably because of the greater activity of the thiophene nucleus, which tends toward the formation of by-products. After isolation, decomposition often occurred under conditions which do not similarly affect the phenyl compounds. For example, phenylthienyl ketone dichloride could not be distilled under reduced pressure without decomposition, whereas benzophenone dichloride is readily purified in such manner. The diphenylcarbinol halides have been made and are moderately stable, but attempts to prepare phenylthienylcarbinol halides resulted in deep-seated decomposition. The reduction of diphenylthienylcarbinol gave only a 50% yield of methane as contrasted with the practically quantitative yield of triphenylmethane from its carbinol. Diphenylthienylcarbinol halides were much less stable than the triphenylcarbinol halides, and the same was true of the corresponding free radicals.

Of novel interest may be noted the preparation of a di-triphenylmethyldithienyl by a peculiar side reaction during a Grignard reaction; and of α-naphthylphenylthienylcarbinol, one of the few asymmetric triarylcarbinols so far described.

Although methods for the preparation of iodothiophene[11] and phenylthienyl ketone[12] already appear in the literature, the yields reported are low. Because these compounds serve as the root compounds for much synthetic work, details are given for obtaining much higher yields.

Iodothiophene, C_4H_3SI.—Thirty-five grams of thiophene and 50 cc. of benzene or petroleum ether were placed in a glass-stoppered wide-mouth bottle. With constant

shaking and cooling when necessary, alternate additions of small amounts of yellow mercuric oxide and iodine were made until totals of 75 g. and 109 g., respectively, had been added. The liquid was then filtered and the solid cake washed with ether. Filtrate and wash were combined, shaken with a dilute solution of sodium thiosulfate to remove excess iodine, dried over calcium chloride, and the solvent was distilled on the water bath. The residue was fractionally distilled under reduced pressure. Iodothiophene distils at 80 to 81° under 20 mm. pressure, or 90 to 94° under 34 to 38 mm. pressure. Yield of 75% of the theoretical was obtained. A small quantity of thiophene was recovered from the ether distillate by treating it with mercuric oxide and dilute acetic acid and decomposing the mercury compound[13] so obtained with conc. hydrochloric acid. This recovery gave an efficiency of 85% on the thiophene actually consumed.

Phenylthienyl Ketone, $C_6H_5COC_4H_3S$.—Anhydrous aluminum chloride (108 g.) was suspended in carbon disulfide (300 g.) in a 3-necked flask. The flask was fitted with a mercury sealed agitator, a reflux condenser and a thermometer dipping into the liquid. Through the condenser was added a mixture of thiophene (60 g.), benzoyl chloride (105 g.) and carbon disulfide (225 g.) over a period of $3^1/_2$ hours. The temperature was kept between 15 and 25° during addition, then stirring was continued at room temperature for three hours, after which the mixture stood over night. In the morning the reaction mass was warmed to reflux temperature for $3^1/_2$ hours, then cooled, poured into ice and extracted with ether. The extract was washed with sodium carbonate solution and water, dried with calcium chloride, and the ether distilled. The residue was distilled under reduced pressure. The ketone boils at 200 to 209° under 30 to 40 mm. pressure. Recrystallized from petroleum ether, it melted at 56 to 57°. The yield was 117 g., which is 87%.

If the thiophene and aluminum chloride were first introduced into the flask with carbon disulfide as diluent, they reacted vigorously. Subsequent addition of benzoyl chloride in carbon disulfide solution gave a sticky crude product, and a low yield of ketone was obtained.

Phenylthienyl Ketone Phenylhydrazone, $C_6H_5C(NNC_6H_5)C_4H_3S$.—Crystals were obtained, after cooling, from a mixture of 1.4 g. ketone, 1 cc. phenyl hydrazine, and 3 cc. 50% acetic acid warmed with sufficient alcohol to effect complete solution. Recrystallized from hot alcohol, the light fawn-colored crystals melted at 91 to 93° and showed a positive qualitative test for nitrogen.

Anal. Calcd. for $C_{17}H_{14}N_2S$: S, 11.52. Found: S, 11.63.

Phenylthienyl Ketone Dichloride, $C_6H_5CCl_2C_4H_3S$.—A mixture of 19 g. of ketone and 22 g. (5% excess) of phosphorus pentachloride was heated at 60 to 80° for one hour. The phosphorus oxychloride formed in the reaction was distilled under reduced pressure and the partial vacuum maintained for one hour in order to remove excess pentachloride. The residual liquid could not be distilled under 20 mm. pressure without decomposition.

Anal. Calcd. for $C_{11}H_8Cl_2S$: Cl, 29.18. Found: Cl, 29.39.

Phenylthienylcarbinol, $C_6H_5CHOHC_4H_3S$.—The procedure of Montagne[14] for reducing a ketone to the corresponding carbinol by means of zinc dust and sodium alcoholate gave a product with sulfur content 3% under the theoretical. The method of Cohen[15] gave good results. To 5 g. of ketone dissolved in 40 cc. of alcohol and 10 cc. of concd. ammonium hydroxide solution was added 10 g. of aluminum amalgam and the mixture was refluxed for six hours. After cooling and filtration, the filtrate was poured into water, whereupon crystals separated after long standing. Recrystallized from ether, the crystals melted at 57 to 58°. Non-identity with the ketone was proved by a mixed melting point.

Anal. Calcd. for $C_{11}H_{10}OS$: C, 69.43; H, 5.30; S, 16.86. Found: C, 69.29; H, 5.23; S, 17.09. *Mol. wt.* Calcd.: 190. Found (cryoscopic in benzene): 195, 187.

Attempts to prepare the carbinol halides by passing dry hydrogen chloride or hydrogen bromide into solutions of the carbinol produced dark-colored oils which evolved gases while drying in a vacuum desiccator, leaving black lava-like solid residues.

Diphenylthienylcarbinol $(C_6H_5)_2C(OH)C_4H_3S$.—This has been described by Thomas[16] and Gomberg and Jickling[8] as prepared from benzophenone and the Grignard reagent from iodothiophene. A slightly higher yield was obtained by synthesis from phenylmagnesium bromide and phenylthienyl ketone, and the product melted at 131°, higher than either of the temperatures previously reported. Condensation of benzophenone dichloride with thiophene in carbon disulfide solution by means of aluminum chloride gave a much lower yield.

When boiled with formic acid[17] the carbinol was reduced to the methane.[18] About half of the carbinol, however, reacted to form a new compound, m. p. 174°, which gave analytical values corresponding to the methane but had a molecular weight of about double that of the methane.

Diphenylthienylcarbinol Bromide $(C_6H_5)_2CBrC_4H_3S$.—A solution of the carbinol in benzene or a suspension in low-boiling petroleum ether was saturated with dry hydrogen bromide. A few lumps of calcium bromide were added to take up the water formed in the reaction. After filtration and evaporation under reduced pressure, crystals of melting point 110 to 111° were obtained. Originally only slightly colored, they quickly turned deep purple, even in a sealed tube in the dark.

Anal. Calcd. for $C_{17}H_{13}BrS$: Br, 24.31. Found: Br, 24.30, 24.09.

Diphenylthienylcarbinol Chloride.[8]—Best results were obtained by suspending the carbinol in petroleum ether with a few lumps of calcium chloride and slowly passing in dry hydrogen chloride to saturation. The solution was evaporated under reduced pressure and the crystals were washed with very small amounts of ice-cold petroleum ether and dried in a current of dry air at room temperature. They melted at 80 to 81° and the yield was 90%. The anilide, $(C_6H_5)_2C_4H_5SCNHC_6H_5$, melts at 118–119°.

After standing for a short time the crystals of the carbinol chloride became colored but no change in the chlorine content could be detected by analysis. No hydrogen chloride was given off when the crystals were held at 65° for twelve hours, or when a benzene solution was held at 65° for twenty-four hours.

Diphenylthienylmethyl.—The free radical was prepared by shaking benzene, bromobenzene or xylene solutions of the chloride or bromide with molecular silver at room temperature. The solutions were immediately colored red. Measurements of the amount of free radical formed by the usual oxygen absorption test[7] gave very erratic results. Depending upon the length of time the sample was left in the apparatus, absorptions ranged from 25 to 200% of the quantity theoretically required for the formation of a peroxide. Determination of the amount of silver chloride formed proved that the metal reacted completely with the halogen.

Attempts to isolate the solid free radical by usual methods gave pink crystals of melting point 157 to 162°, which gave oxygen absorptions of only 20% of the calculated value. The general behavior of this free radical was very much like that of phenylthioxanthyl.

5,5′-Di-triphenylmethyl-2,2′-dithienyl, $(C_6H_5)_3CC_4H_2SC_4H_2SC(C_6H_5)_3$.—Triphenylthienylmethane was made by Weisse[19] from triphenylcarbinol and thiophene with phosphorus pentoxide as condensing agent. An attempt was made to prepare this compound from triphenylchloromethane and the Grignard reagent of iodothiophene, by analogy to the method for making tetraphenylmethane.[20] Besides quantities of triphenylmethyl peroxide and triphenylmethane, a new product was obtained, in 5

to 40% yields, which was not the methane of Weisse. The latter melts at 237°, whereas the new substance melted at 277°, after recrystallizing from ethylene dibromide.

The structure of this new product was established by its synthesis from triphenyliodothienylmethane through the Ullmann condensation, using copper-bronze.

$$2(C_6H_5)_3CC_4H_2SI + Cu \longrightarrow (C_6H_5)_3CC_4H_2SC_4H_2SC(C_6H_5)_3 + CuI_2$$

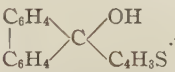
The 5,5'-positions of the triphenylmethyl groups in the thiophene rings have not been proved, but rest on the assumptions of Weisse for the constitution of the products of his phosphorus pentoxide condensations.

Two grams of triphenyliodothienylmethane was mixed with an equal volume of white sand, placed in a small flask and heated in a sulfuric acid bath to 200°. As the temperature rose further, 2 g. of copper–bronze was gradually added with stirring. When the temperature reached 250°, the flask was removed, cooled and the contents extracted with hot benzene. Concentration of the benzene extract gave a 90% yield of crystals of melting point 277°. Comparison of physical properties, solubilities and mixed melting point proved the identity of this compound with that from the Grignard condensation. Inasmuch as the latter reaction was carried out in an atmosphere of hydrogen, the formation of the dithienyl required an oxidation at the expense of part of the reacting compounds.

The dithienyl gave no color with concd. sulfuric acid, was markedly insoluble in most solvents in the cold and was moderately soluble in hot carbon tetrachloride, ethyl acetate, naphthalene, nitrobenzene, bromoform, chloroform and benzene.

Anal. Calcd. for $C_{46}H_{34}S_2$: C, 84.88; H, 5.27; S, 9.86. Found: C, 84.85, 84.48; H, 5.62, 5.43; S, 9.81, 9.79. *Mol. wt.* Calcd.: 650. Found:* 670 (benzene); 668 (chloroform).

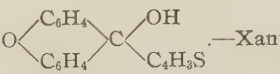
Upon bromination in boiling carbon tetrachloride solution, a dibromo compound, of melting point 287°, was obtained.

Biphenylenethienylcarbinol,  .—To the Grignard reagent from iodothiophene and magnesium in ether was added a benzene–ether solution of fluorenone. The light green precipitate which formed was filtered, washed and treated with ice and acetic acid. The crude carbinol was extracted with ether, washed with sodium carbonate solution and water and dried. After evaporation of the solvent, the oil was recrystallized from petroleum ether. Colorless crystals of melting point 81 to 82° were obtained. After long standing they turned green.

Anal. Calcd. for $C_{17}H_{12}OS$: C, 77.24; H, 4.58; S, 12.13. Found: C, 76.89; H, 4.62; S, 12.20.

α-Naphthylphenylthienylcarbinol $(C_{10}H_7)(C_6H_5)(C_4H_3S)COH$.—α-Naphthylphenyl ketone in ethereal solution was treated with thienylmagnesium iodide. The precipitate was washed, iced and steam distilled. The residue from the distillation was recrystallized from a mixture of ether and petroleum ether, giving colorless crystals with a melting point of 131°.

Anal. Calcd. for $C_{21}H_{16}OS$: C, 79.71; H, 5.10; S, 10.14. Found: C, 79.65; H, 4.92; S, 10.20.

Thienylxanthenol,  .—Xanthone was added in small quantities to the ether solution of thienylmagnesium iodide. The reaction was sluggish and re-

*By ebullioscopic method of Menzies and Wright, *J. Am. Chem. Soc.*, **43**, 2314 (1921).

quired warming. The yellow precipitate was filtered, iced and extracted with ether. Concentration of the extract and recrystallization from ethyl acetate gave a product with melting point of 168 to 169°.

Anal. Calcd. for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.32; S, 11.44. Found: C, 72.78; H, 4.28; S, 11.42.

Thienylxanthenol chloride was made by passing dry hydrogen chloride into a solution of the carbinol in ethyl acetate. Without isolating the chloride, solutions of metal halides in ethyl acetate were added and the following double salts were obtained: $C_{17}H_{11}OSCl \cdot FeCl_3$, bronze plates, m. p. 198°; $C_{17}H_{11}OSCl \cdot HgCl_2$, small red crystals, melting with decomposition at 182 to 198°, varying with the rate of heating; $C_{17}H_{11}OSCl \cdot ZnCl_2$, red crystals, m. p. 225 to 227°.

Summary

1 The work of Schlenk and Renning upon the free radical, phenylthioxanthyl, has been checked, and grounds offered for rejection of their determination of its molecular weight.

2 The free radical, diphenylthienylmethyl, has been prepared in solution and studies made of its stability.

3 From the detailed study of these two triarylmethyls containing sulfur, it appears that the presence of a bivalent ring-sulfur atom in its molecule does not interfere with the formation of a free radical in solution; but that it does greatly enhance the tendency toward isomerization and polymerization of the radical. Hence the isolation of the solid radical is made difficult or even impossible.

4 Some thiophene analogs of di-, tri- and tetra-phenylmethane compounds have been synthesized.

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